

# Configuration of 3-Substituted 1-Chloropropenes

By W. C. WOLFE,<sup>1</sup> H. M. DOUKAS<sup>2</sup> AND J. S. ARD

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The configuration of the 1,3-dichloropropenes remained ambiguous even though considerable work had been done in an attempt to establish the structure of the two isomeric forms by means of relative reactivities<sup>3</sup> or by means of physical data,<sup>4</sup> until Hatch and Perry<sup>5</sup> succeeded in chemically transforming each isomer into a compound whose configuration had been established previously. Later work<sup>6</sup> on relative reactivities substantiated the chemical work of Hatch and Perry.<sup>5</sup> A further aid in the establishment of structure of the 1,3-dichloropropenes was encountered in the preparation of compounds in the 1-naphthalene series to be used in plant-growth regulator investigations.<sup>7</sup>

When the 1-naphthylmagnesium bromide reacted with 1,3-dichloropropene, 3-(1-naphthyl)-1-chloro-1-propene was obtained as a product<sup>8</sup> but no mention was made of the possibility of *cis-trans* isomerism. Harris<sup>9</sup> pointed out that two isomers were obtained in this reaction, a white solid melting at 50° and a pale yellow liquid boiling at 155–160° (6–7 mm.). He concluded that he had the *cis*- and *trans*-isomers of 3-(1-naphthyl)-1-chloro-1-propene and, from dipole moment studies conducted by Lander and Svirbely,<sup>10</sup> tentatively assigned the following configurations; solid isomer *trans*, liquid isomer *cis*. However, he made no effort to start with *cis*-1,3-dichloropropene and correlate that product with the corresponding naphthyl product.

The work of Hatch and Perry<sup>5</sup> established the isomeric forms of 1,3-dichloropropene as follows: low boiling isomer I, *cis*-configuration; high boiling isomer II, *trans*-configuration. Starting with pure *cis*-1,3-dichloropropene (I) and converting it to the 3-(1-naphthyl)-1-chloro-1-propene by way of the Grignard reaction, we obtained a white solid III as a product, while the *trans*-isomer (II) gave a liquid product (IV). This seemed at variance with the work of Harris<sup>9</sup> for the assignment of configuration to the 3-(1-naphthyl)-1-chloro-1-propenes. For this reason, dipole moment measurements on all these isomeric compounds were repeated (Table I) and, although possibly not of a conclusive na-

ture, they show a correlation of the *cis-trans*-1,3-dichloropropenes with the isomeric 3-(1-naphthyl)-1-chloro-1-propenes.

TABLE I

DIPOLE MOMENTS OF 1,3-DICHLOROPROPENE AND 3-(1-NAPHTHYL)-1-CHLORO-1-PROPENE ISOMERS

Compounds	Debye units		Con-figuration
1,3-Dichloropropene			
104° isomer (I)	1.92 (4a)	..	1.85 <sup>11</sup> <i>cis</i>
112° isomer (II)	1.73 (4a)	..	1.74 <sup>11</sup> <i>trans</i>
3-(1-Naphthyl)-1-chloro-1-propene			
Solid isomer (III)	..	1.27(9,10)	1.60 <sup>11</sup> <i>cis</i>
Liquid isomer (IV)	..	1.47(9,10)	1.39 <sup>11</sup> <i>trans</i>

The infrared spectra of these compounds (Fig. 1) also are interpreted to indicate that the solid isomer of 3-(1-naphthyl)-1-chloropropene is the *trans* form, at variance with the work of Harris.<sup>9</sup> To aid in the interpretations, the curves of *cis*- and *trans*-3-chloropropenoic acid are shown also. The configuration correlations applying to simple ethylenic groups did not seem applicable because of the effect of an adjacent halogen atom in all cases, and of the complexity from aromatic unsaturation in some. However, a band near 7.5  $\mu$  consistently was of prominent intensity in all the isomers assigned the *cis*-configuration, and this was either absent or very weak in all the remaining (*trans*) isomers. Because other nearby spectral patterns correspond to a recognizable extent in the respective isomers, this 7.5  $\mu$  band stands out as an additional band, which indicates a mode of origin prominent in only one (*cis*) of the isomeric forms. At wave lengths this short, bands of such intensity characteristically have stable positions representing identical portions of varied molecules, and are unlikely to appear randomly from other causes. The group in common for which it seems characteristic, when weak or absent in the opposite isomer, is the *cis*-form of Cl-CH=CH-C. A consideration of the spectra of other halogenated ethylenic substances indicated that neither of the two hydrogen atoms should be substituted if strict consistency with these examples is to be expected, though the nearby region seems promising as a source of similar correlations.

Spectral correlation of I and III, and correspondingly of II and IV, seems to exclude any possibility of abnormal reaction with the Grignard reagent, thus confirming the conclusion reached by Kirmann<sup>12</sup> that the reaction occurs in the normal way, with the reactive chloride attached to the single-bonded carbon atom.

## Experimental

**1,3-Dichloropropenes.**—Commercial samples of the mixed isomers were distilled at a slow rate at atmospheric pressure and the *cis*- and *trans*-isomers boiling at 104.5–105.0° (I) and 110–111° (II), respectively, were collected.

**3-(1-Naphthyl)-1-chloro-1-propenes.**—The method of Bert and Dorier<sup>8</sup> was used to prepare the *cis*- and *trans*-isomers. *cis*-1,3-Dichloropropene (I) was treated with 1-naphthylmagnesium bromide to give a solid isomer (III)

(12) A. Kirmann, Pacaud and H. Dosque, *Bull. soc. chim.*, [5] 1, 890 (1934); A. Kirmann, *ibid.*, [4] 47, 834 (1930).

- (1) National Bureau of Standards, Washington, D. C.
- (2) Part of a Thesis presented by H. M. Doukas to Georgetown University, Washington, D. C., in partial fulfillment of the requirements for the degree of M.S.
- (3) (a) L. F. Hatch and G. B. Roberts, *THIS JOURNAL*, **68**, 1196 (1946); (b) L. J. Andrews and R. E. Kepner, *ibid.*, **69**, 2230 (1947); (c) L. F. Hatch, L. B. Gordon and J. J. Russ, *ibid.*, **70**, 1093 (1948).
- (4) (a) H. A. Smith and W. H. King, *ibid.*, **70**, 3528 (1948); (b) R. A. Oriani and C. P. Smyth, *J. Chem. Phys.*, **16**, 930 (1948); (c) A. Kirmann, *Bull. soc. chim.*, **6**, 841 (1939); (d) W. West and M. Farnsworth, *Trans. Faraday Soc.*, **27**, 145 (1931).
- (5) L. F. Hatch and R. H. Perry, Jr., *THIS JOURNAL*, **71**, 3262 (1949).
- (6) (a) L. F. Hatch, A. N. Brown and H. P. Bailey, *ibid.*, **72**, 3198 (1950); (b) H. Pourrat and R. Schmitz, *Bull. soc. chim.*, 505 (1952).
- (7) H. M. Doukas, W. C. Wolfe and T. D. Fontaine, *J. Org. Chem.*, in press.
- (8) L. Bert and P. C. Dorier, *Bull. soc. chim.*, **37**, 1690 (1925); *ibid.*, **39**, 1610 (1926).
- (9) T. H. Harris, M.S. Thesis, George Washington University Washington, D. C., 1943.
- (10) J. J. Lander and W. J. Svirbely, *THIS JOURNAL*, **66**, 235 (1944).
- (11) Measurements were kindly made by Dr. A. Maryott, National Bureau of Standards, Washington, D. C.

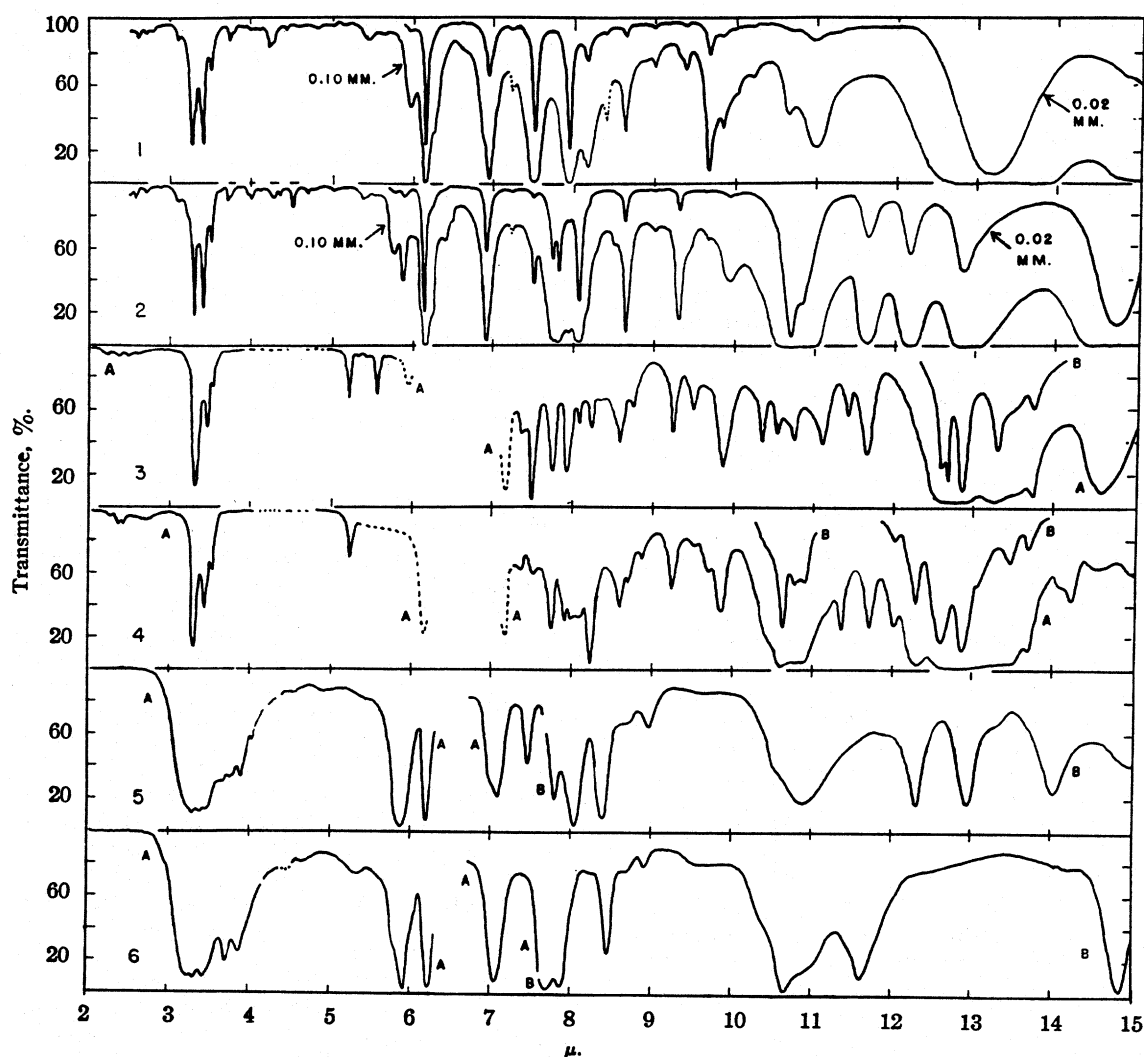


Fig. 1.—Infrared curves of substituted *cis*- and *trans*-chloropropenes. Curves 1 and 2 were obtained with a Perkin-Elmer instrument Model 21; curves 3-6 with Model 12 C: 1, 1,3-dichloropropene (I), b.p. 104.5°,  $n_D^{20}$  1.4670, interpreted to be the *cis*-form, liquid state; 2, 1,3-dichloropropene (II), b.p. 110-111°,  $n_D^{20}$  1.4740, interpreted to be the *trans*-form, liquid state; 3, 3-(1-naphthyl)-1-chloro-1-propene (III) solid isomer, m.p. 50-51°, interpreted to be the *cis*-form, 0.55-mm. cell, A-10% in  $CS_2$ , B-1% in  $CS_2$ ; 4, 3-(1-naphthyl)-1-chloro-1-propene (IV), liquid isomer, interpreted to be the *trans*-form, 0.55-mm. cell, A-10% in  $CS_2$ , B-1% in  $CS_2$ ; 5, 3-chloropropenoic acid (V), m.p. 63-64°, *cis*-form, 0.55-mm. cell, A-2% in  $CCl_4$ , B-2% in  $CS_2$ ; 6, 3-chloropropenoic acid (VI), m.p. 84-85°, *trans*-form, 0.55-mm. cell, A-2% in  $CCl_4$ , B-2% in  $CS_2$ .

(*cis*) in 48% yield, m.p. 50-51°, b.p. 132-134° (1.4-1.7 mm.). From II a liquid isomer (IV) (*trans*) was obtained in 38% yield, b.p. 137-145° (2.5 mm.).

**3-Chloropropenoic Acids.**—The *cis* (V) and *trans* (VI) isomers, m.p. 63-64° and 84-85°, respectively (lit. 63-64°, 85.5-86°<sup>13</sup>), were prepared by the method of Backer and Beute<sup>13</sup> from 2-propynoic acid.

EASTERN REGIONAL RESEARCH LABORATORY<sup>14</sup>  
PHILADELPHIA 18, PENNSYLVANIA

(13) H. J. Backer and A. E. Beute, *Rec. trav. chim.*, **54**, 167 (1935).

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